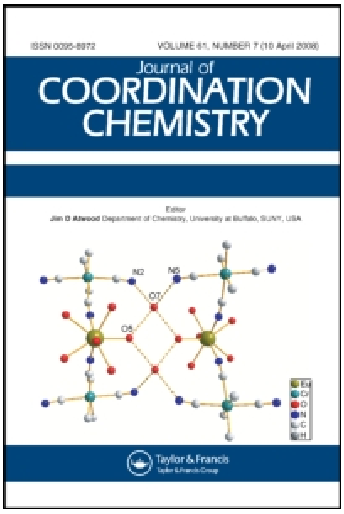

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MOLECULAR RECOGNITION OF AN ORGANIC MOLECULE THROUGH A TWO DIMENSIONAL SQUARE NETWORK INCLUSION COMPLEX. SYNTHESIS AND CRYSTAL STRUCTURE OF [Cd(4,4'-bpy)$_2$(H$_2$O)$_2$] (BF$_4$)$_2$ · 2(4,4'-bpy) · (C$_6$H$_6$N$_2$O$_2$) · 2H$_2$O

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MOLECULAR RECOGNITION OF AN ORGANIC MOLECULE THROUGH A TWO DIMENSIONAL SQUARE NETWORK INCLUSION COMPLEX. SYNTHESIS AND CRYSTAL STRUCTURE OF $[Cd(4,4'\text{-bpy})_2(H_2O)_2](BF_4)_2 \cdot 2(4,4'\text{-bpy}) \cdot (C_6H_6N_2O_2) \cdot 2H_2O$

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The 2D square network complex $[Cd(4,4'\text{-bpy})_2(H_2O)_2]$ $(BF_4)_2 \cdot 2(4,4'\text{-bpy}) \cdot (C_6H_6N_2O_2) \cdot 2H_2O$ (**1**) (where 4,4′-bpy = 4,4′-bipyridine and $C_6H_6N_2O_2$ = *o*-nitrobenzenamine) has been prepared by reaction of $Cd(BF_4)_2 \cdot 6H_2O$ and 4,4′-bpy in the presence of *o*-nitrobenzenamine. High shape selectivity was observed in this self-assembly process. Single crystal X-ray analysis revealed that **1** possesses a 2D square network of $[Cd(4,4'\text{-bpy})_2(H_2O)_2]$ cations, which are made up of layers stacked upon each other. The *o*-nitrobenzenamine molecule is 2-fold disordered over a centre of inversion in the same plane as the cationic network. Uncoordinated 4,4′-bpy molecules as well as uncoordinated water molecules and BF_4^- counter anions are intercalated between the cationic network layers. Extensive hydrogen-bonding is observed to stabilize this crystal packing.

Keywords: Cadmium(II); 4,4′-bipyridine; molecular recognition; crystal structure; self-assembly; coordination polymer

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INTRODUCTION

Self-assembly of molecular components in the form of extended solids is a powerful method in the design of new inclusion compounds[1] and quite attractive since cyclization of a large molecule by the usual synthetic methods is a tedious and low-yield process.[2] The specific effect in these inclusion compounds has been attributed to steric exclusion, hydrophobic interactions, dispersion interactions, *etc.*[3] Generally, weak interaction allow the assembly processes to proceed under reversible conditions, thus favouring the formation of regular structures. With the development of new materials, more and more novel, conformationally rigid macrocycles have emerged.[2,4] Fujita and coworkers have reported a two-dimensional (2D) square network inclusion compound $[Cd(4,4'\text{-bpy})_2(NO_3)_2]\cdot(Br_2C_6H_4)_2$, in which interaction between host and guest is through electrostatic attraction.[5] However, this kind of inclusion compound incorporating guest molecules through hydrogen bonds is relatively unexplored. Here we report the molecular recognition of *o*-nitrobenzenamine through a 2D square network complex and the crystal structure of $[Cd(4,4'\text{-bpy})_2(H_2O)_2](BF_4)_2\cdot 2(4,4'\text{-bpy})\cdot(C_6H_6N_2O_2)\cdot 2H_2O$ in which guest molecules are incorporated through hydrogen bonds.

EXPERIMENTAL

Synthesis of $[Cd(4,4'\text{-bpy})_2(H_2O)_2](BF_4)_2\cdot 2(4,4'\text{-bpy})\cdot(C_6H_6N_2O_2)\cdot 2H_2O$

All materials were of reagent grade and were used without further purification. Doubly distilled water was used throughout this work. The compound $\{[Cd(4,4'\text{-bpy})_2(H_2O)_2](BF_4)_2\cdot 2(4,4'\text{-bpy})\cdot(C_6H_6N_2O_2)\cdot 2H_2O\}$ was prepared by refluxing an methanol-water solution (v/v 1.5 : 1 40 cm^3) of $Cd(BF_4)_2\cdot 6H_2O$ (1.0 mmol), 4,4′-bpy (4.0 mmol) and 2-nitrobenzenamine (1.5 mmol) for 1h. Yellow single crystals suitable for X-ray crystal structure determination were obtained by slow evaporation at room temperature over a few weeks. Yield 80%. *Anal.*, Calc. For $C_{46}H_{46}B_2N_{10}O_6F_8Cd$ (%): C, 49.3; H, 4.1; N, 12.5. Found: C, 49.0; H, 4.2; N, 12.1.

Elemental analyses for C, H, N were performed on a Perkin-Elmer 240 instrument. IR spectra was recorded in KBr pellets in the range 4000–400 cm^{-1} using a Nicolet 170 SXFTIR spectrophotometer. Thermogravimetric and differential thermal analyses were performed on a simultaneous SDT 2960 thermal analyzer under flowing N_2 with a heating rate of 10 °C/min.

X-Ray Crystallographic Analysis

A yellow block shaped crystal of approximate dimensions 0.3 × 0.3 × 0.2 mm was selected for X-ray analysis and mounted on an Enraf-Nonius CAD4 diffractometer. A summary of crystal data collection parameters are listed in Table I. Unit cell parameters were measured by a least-squares method based on the setting angles of 25 carefully centred reflection with 2θ values between 12° and 20°. Intensity data were measured using the ω–2θ scan technique. Of the 4306 independent reflections ($R_{int} = 0.090$), 2642 reflections observed with $I > 2\sigma(I)$ were used in the structure solution and refinement. Intensity data were corrected for Lorentz-polarization effects and absorption based on ψ-scan data.

The structure was solved by Patterson methods using the SHELXS 86 program[6] and refined using SHELXL 93.[7] A total of 296 parameters with non-hydrogen atoms anisotropic were refined by full-matrix least-squares methods on F_o^2, where $w = 1/[\sigma^2(F_o^2) + (0.1209P)^2$ and $P = (F_o^2 + 2F_c^2)/3$. Refinement converged at $R = 0.079$, $R_w = 0.190$ ($I \geq 2\sigma(I)$ observed data); $R = 0.127$, $R_w = 0.218$ (all data). The 2-nitrobenzenamine molecule is

TABLE I Summary of crystal data, details of intensity collection and least-square refinement parameters for $[Cd(4,4'\text{-bpy})_2(H_2O)_2]\,(BF_4)_2 \cdot 2(4,4'\text{-bpy}) \cdot (C_6H_6N_2O_2) \cdot 2H_2O$

Empirical formula	$C_{46}H_{46}B_2N_{10}O_6F_8Cd$
Mr	1120.95
Crystal syst	Monoclinic
Space group	$C2/c$
T, K	300(2)
a, Å	17.844(1)
b, Å	11.848(1)
c, Å	23.502(2)
β, deg	99.00(1)
V, Å^3	4907.5(6)
Z	4
$D_{calc.}$ g cm^{-3}	1.517
$\mu(M_oK_\alpha)$, cm^{-1}	5.34
$F(000)$	2280
Range θ collect, deg	1.75–24.98
Absorption correction	ψ-scan
Max. and min. transmission factors	0.899 and 0.850
No. of reflcns collcd	8376
No. of indep. reflcns	4306
Data/restraints/parameters	4306/10/296
R_{int}	0.090
Final R [$I > 2\sigma(I)$]	$R = 0.079$, $R_w = 0.1900$
R indices (all data)	$R = 0.1268$, $R_w = 0.2178$
GOF [$I > 2\sigma(I)$]	1.099
GOF (all data)	0.977
Smallest/largest peak in final difference map (e/Å)	− 1.221/1.050

disordered on a centre of inversion and all the atoms were refined isotropically with occupancies of 0.5. N6 of the nitro group of one half occupancy overlaps with the ring carbon at the *para*-position of the other centrosymmetric half of the molecule (C25) and were refined as mixed

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[\text{Cd}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2 \cdot 2(4,4'\text{-bpy}) \cdot (\text{C}_6\text{H}_6\text{N}_2\text{O}_2) \cdot 2\text{H}_2\text{O}$

Atom	*x/a*	*y/b*	*z/c*	$U_{(eq)}$[a]
Cd	0	−249(1)	7500	27(1)
O(1)	−1265(3)	−182(5)	7125(2)	45(1)
O(4)	2479(4)	−357(7)	2357(3)	75(2)
N(1)	0	1780(8)	7500	37(2)
N(2)	0	−2243(7)	7500	34(2)
N(3)	192(4)	−304(7)	6517(3)	37(2)
N(4)	8088(6)	3158(10)	3223(4)	74(3)
N(5)	8386(6)	726(10)	6012(4)	71(3)
C(1)	−625(5)	−2827(7)	7291(3)	34(2)
C(2)	−644(5)	−3990(7)	7281(4)	39(2)
C(3)	0	−4569(8)	7500	31(3)
C(4)	0	4171(10)	7500	36(3)
C(5)	−660(5)	3549(7)	7515(4)	40(2)
C(6)	−634(5)	2369(8)	7502(4)	41(2)
C(7)	527(5)	517(8)	6274(4)	47(2)
C(8)	477(6)	654(9)	5691(4)	52(3)
C(9)	57(5)	−64(6)	5318(3)	33(2)
C(10)	−271(7)	−960(8)	5571(4)	61(3)
C(11)	−180(7)	−1037(8)	6163(4)	56(3)
C(12)	8040(8)	211(13)	5540(5)	91(4)
C(13)	7983(8)	628(11)	4992(5)	79(4)
C(14)	8299(5)	1655(8)	4900(4)	43(2)
C(15)	8234(5)	2155(8)	4311(4)	47(2)
C(16)	7894(7)	1623(8)	3823(4)	63(3)
C(17)	7847(8)	2140(10)	3305(4)	70(3)
C(18)	8407(9)	3692(13)	3685(6)	103(5)
C(19)	8499(9)	3219(11)	4233(6)	101(5)
C(20)	8667(6)	2192(10)	5380(4)	61(3)
C(21)	8697(6)	1698(11)	5909(4)	61(3)
O(2)	5655(17)	227(24)	3939(12)	144(9)
O(3)	4767(17)	1248(25)	3891(12)	152(10)
N(6)	5145(11)	408(16)	4163(8)	132(6)
N(7)	6064(16)	−1077(24)	4880(12)	110(8)
C(22)	5038(14)	238(22)	4712(10)	69(6)
C(23)	4466(10)	679(14)	4935(8)	106(5)
C(24)	4361(20)	479(30)	5498(16)	112(10)
C(25)	4855(11)	−408(16)	5837(8)	132(6)
C(26)	5416(19)	−801(27)	5580(15)	97(9)
C(27)	5534(10)	−679(14)	5065(8)	106(5)
B	7434(6)	−2809(8)	6124(4)	184(12)
F(1)	8122(6)	−2318(10)	6115(6)	209(3)
F(2)	7125(7)	−2375(10)	6572(5)	209(3)
F(3)	6968(7)	−2613(10)	5618(4)	209(3)
F(4)	7537(7)	−3939(8)	6208(5)	209(3)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atoms. The two carbon atoms (C23 and C27) at *ortho*-positions to the nitro group of both disordered molecules coincide and hence have occupancies of 1.0. The F atoms in BF_4^- are also disordered, causing large residual peaks and holes in the final difference map. The B–F and F–F distances were fixed and the displacement parameters of the F atoms were restrained to be the same in refinement. Hydrogen atoms of the bipy ligands and molecules were generated geometrically and were assigned to ride on the parent carbon atoms. Four hydrogen atoms located from the difference map were not refined but included in the structure factor calculation. All non-H atoms were refined anisotropically except the disordered ones which were refined isotropically. Final atomic coordinates are listed in Table II.

RESULTS AND DISCUSSION

Preparation

When suitable guest molecules such as *o*-nitrobenzenamine are present, reaction of $Cd(BF_4)_2 \cdot 6H_2O$ and 4,4′-bpy in MeOH-H_2O yields a 2D square network inclusion compound $[Cd(4,4'\text{-bpy})_2(H_2O)_2]\,(BF_4)_2 \cdot 2(4,4'\text{-bpy}) \cdot (C_6H_6N_2O_2) \cdot 2H_2O$, similar to the reaction of $Cd(NO_3)_2$ and 4,4′-bpy in the presence of *o*-dibromobenzene to form $[Cd(4,4'\text{-bpy})_2(NO_3)_2] \cdot (Br_2C_6H_4)_2$.[5] This self-assembly process exhibits high shape selectivity. While *o*-nitrobenzenamine was assembled efficiently, 4-methyl-5-nitrobenzenamine, 4-methyl-2-nitrobenzenamine, 2-methyl-4-nitrobenzenamine, 5-methoxy-2-methyl-5-nitrobenzenamine, *m*-nitrobenzenamine and *p*-nitrobenzenamine were not recognized. This discrimination of isomers in the clathration could be utilized to separate *o*-nitrobenzenamine from the isomer mixtures as previously suggested.[5,8–10] Thus treatment of a mixture of *o*-, *m*- and *p*-nitrobenzenamine (1 : 1 : 1) with $Cd(BF_4)_2 \cdot 6H_2O$ and 4,4′-bpy in methanol-water yielded only **1** as inclusion crystals, from which *o*-nitrobenzenamine could be recovered by acidic decomposition of **1** followed by recrystallization.

Description of the Structure

The structure of **1** consists of discrete square network $[Cd(4,4'\text{-bpy})_2(H_2O)_2]$ cations, ClO_4^- anions, uncoordinated 4,4′-bpy molecules, *o*-nitrobenzenamine molecules and uncoordinated water molecules. An ORTEP drawing of the structure around the cadmium in **1** with the atom numbering scheme is shown in Figure 1. Packing of the molecules in the unit cell is

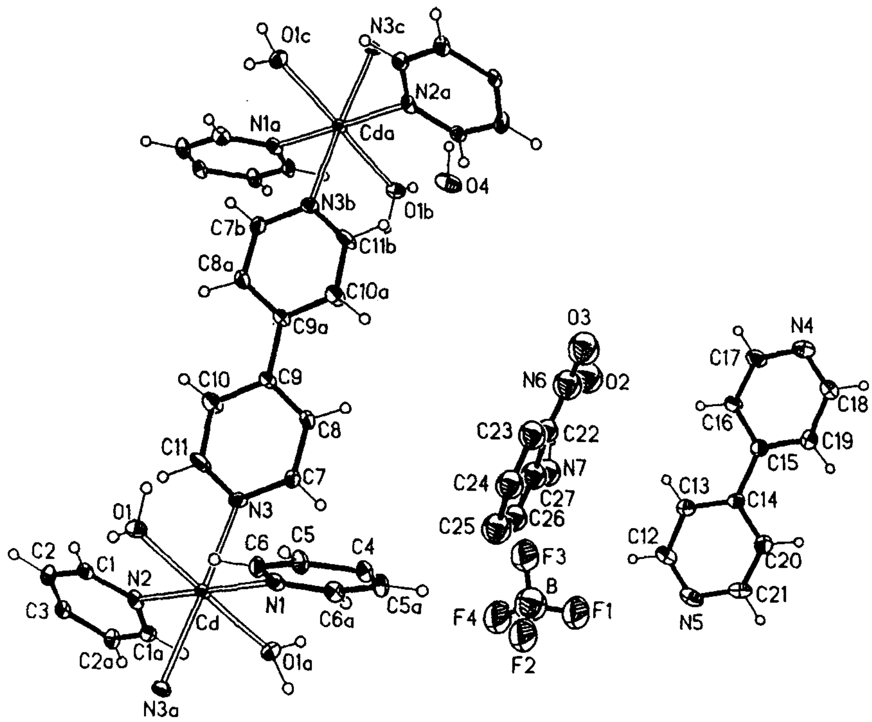

FIGURE 1 The structure around the cadmium atom in [Cd(4,4′-bpy)$_2$(H$_2$O)$_2$] (BF$_4$)$_2$ · 2(4,4′-bpy) · (C$_6$H$_6$N$_2$O$_2$) · 2H$_2$O with the atom numbering scheme.

shown in Figure 2. Selected bond lengths and angles are collected in Table III. The cadmium ion is located on a 2-fold rotation axis and exhibits a slightly distorted octahedral geometry with four pyridine nitrogen atoms at the equatorial positions and two *trans* water molecules at the apical positions. This local coordination geometry is very similar to that in [Cd(4,4′-bpy)$_2$(H$_2$O)$_2$](PF$_6$)$_2$ · 2(4,4′-bpy) · 4H$_2$O[11] but a little different from that in [Cd(4,4′-bpy)$_2$(NO$_3$)$_2$] · (Br$_2$C$_6$H$_4$)$_2$,[5] in which two nitrate ions take the place of two water molecules occupying the apical positions. The Cd–N bond distances (average 2.385 Å) are slightly longer than those in [Cd(4,4′-bpy)$_2$(NO$_3$)$_2$] · (Br$_2$C$_6$H$_4$)$_2$ (average 2.366 Å), whereas the bond distances Cd–Ow (2.292(6) Å) fall in the normal range.[11] The N2–Cd–N1 bond angle is 180.000(2)° whereas N3–Cd–N3$^{\#3}$ ($^{\#3}$ $-x, y, -z+3/2$) bond angle (176.9(2)°) deviates from 180°, indicating the 2D square network of [Cd(4,4′-bpy)$_2$ (H$_2$O)$_2$] consists of a linear "warp" and a zigzag "weft". In addition, only half of the coordinated 4,4′-bpy molecules are completely planar, while the others have a dihedral angle of 26.2(3)° between the two pyridyl rings. This

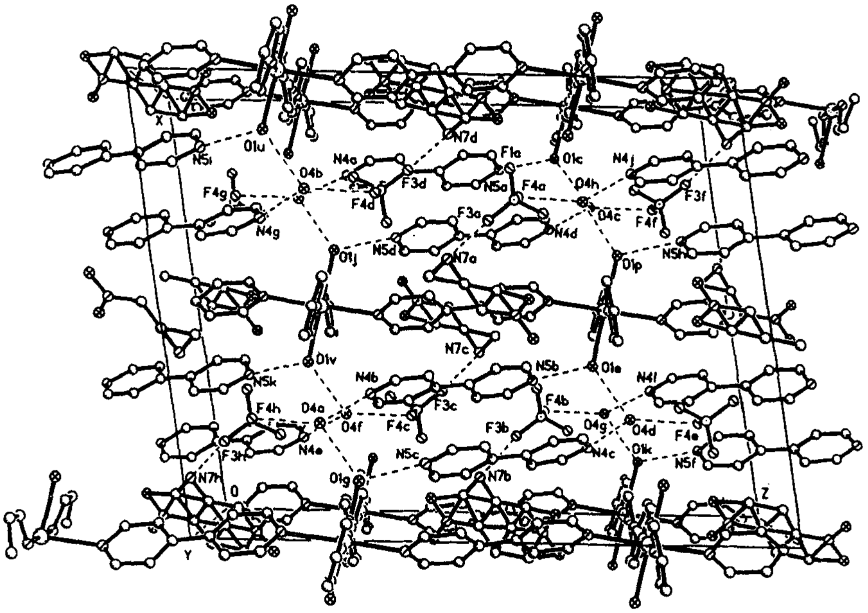

FIGURE 2 Projection down the *b* axis of $[Cd(4,4'\text{-bpy})_2(H_2O)_2]$ $(BF_4)_2 \cdot 2(4,4'\text{-bpy}) \cdot (C_6H_6N_2O_2) \cdot 2H_2O$.

TABLE III Selected bond lengths (Å) and bond angles (deg) for $[Cd(4,4'\text{-bpy})_2(H_2O)_2](BF_4)_2 \cdot 2(4,4'\text{-bpy}) \cdot (C_6H_6N_2O_2) \cdot 2H_2O$

Bond lengths (Å)			
Cd–O1	2.292(6)	Cd–N2	2.362(9)
Cd–N3	2.388(6)	Cd–N1	2.404(10)
N1–C6	1.330(10)	N2–C1	1.339(9)
N3–C11	1.310(11)	N4–C17	1.305(14)
N5–C12	1.33(2)	N6–C22	1.35(3)
N7–C27	1.20(3)	C3–C4$^{\#1}$	1.493()
C9–C9$^{\#2}$	1.49(2)	C14–C15	1.494(12)
O2–N6	1.14(3)	O3–N6	1.31(3)
Bond angles (deg)			
O1$^{\#3}$–Cd–O1	176.0(3)	O1–Cd–N2	92.0(2)
O1–Cd–N3	84.9(2)	N2–Cd–N3	88.4(2)
O1–Cd–N3$^{\#3}$	95.3(2)	N3–Cd–N3$^{\#3}$	176.9(2)
O1–Cd–N1	88.0(2)	N2–Cd–N1	180.000(3)
N3–Cd–N1	91.6(2)	C11–N3–Cd	119.8(6)
C7–N3–Cd	122.9(6)	C5–C4–C3$^{\#4}$	121.9(5)
Hydrogen bond distances (Å)			
O1–HO1a···O4′	2.722	O1–HO1b···N5″	2.805
O2···H7a–N7	2.704	O4···N4‴	2.781
O4–H4···F4*	2.842	N7···F3	2.836

$^{\#1}x, y-1, z$; $^{\#2}-x, -y, -z+1$; $^{\#3}-x, y, -z+3/2$; $^{\#4}x, y+1, z$; $'-x, -y, 1-z$; $''-1+x, y, z$; $'''-1/2+x, -1/2+y, z$; $^{*}-1/2+x, -1/2-y, -1/2+z$.

difference is most likely due to host-guest interactions as previously suggested in $[Cd(4,4'\text{-}bpy)_2](NO_3)_2(C_6H_4Br_2)_2$.[5]

The cationic $[Cd(4,4'\text{-}bpy)_2(H_2O)_2]$ square network is parallel to the *bc* plane and each network is made up of layers stacked upon each other. Unlike the case in $[Cd(4,4'\text{-}bpy)_2(H_2O)_2](PF_6)_2 \cdot 2(4,4'\text{-}bpy) \cdot 4H_2O$,[11] two uncoordinated 4,4′-bpy molecules in compound **1** are not clathrated into each square cavity; they are simply intercalated between the cationic network layers as well as the uncoordinated water molecules and BF_4^- anions. The *o*-nitrobenzenamine molecule is 2-fold disordered over a centre of inversion in the same plane as the cationic network planes. In $[Cd(4,4'\text{-}bpy)_2](NO_3)_2(C_6H_4Br_2)_2$ the guest molecules of $Br_2C_6H_4$ are clathrated into the cavities of square network without disorder.[5]

The crystal packing is stabilized by extensive hydrogen bonding. The *o*-nitrobenzenamine molecule is connected with BF_4^- anions by hydrogen-bonding (N7 ··· F3 2.836 Å), while the BF_4^- anion is hydrogen bonded to the uncoordinated water molecule (O4–H4 ··· F4* 2.842 Å, symmetry code: $-1/2+x, -1/2-y, -1/2+z$). The uncoordinated water molecule connects with both coordinated water molecule (O1–HO1a···O4′ 2.722 Å, symmetry code: $-x, -y, 1-z$) and uncoordinated 4,4′-bpy molecules (O4···N4‴ 2.781 Å, symmetry code: $''' -1/2+x, -1/2+y, z$). The other nitrogen atom (N5) in the uncoordinated 4,4′-bpy molecule is hydrogen bonded to a coordinated water molecule in the nearest-neighbor $[Cd(4,4'\text{-}bpy)_2(H_2O)_2]$ square network (O1–HO1b···N5″ 2.805 Å, symmetry code: $'' -1+x, y, z$). Furthermore, an intramolecular hydrogen bond in the *o*-nitrobenzenamine molecule was observed (O2···H7a–N7 2.704 Å).

IR Spectra and Thermogravimetric Analysis

In the IR spectra, there are at least five bands in the 3000–3500 cm^{-1} region. The band at 3056 cm^{-1} may be attributed to the C–H stretch of the pyridine ring. Two sharp bands at 3460 cm^{-1} and 3366 cm^{-1} should be assigned to the NH_2 group of *o*-nitrobenzenamine in compound **1**. Two broad bands at 3266 and 3139 cm^{-1} must be attributed to H–O–H vibrations of the water molecule; they occur at relatively lower wave numbers indicating the existence of hydrogen bonding interactions.[12] This is in accordance with the the X-ray structure.

The TDA curve of compound **1** (Figure 3) shows seven endotherms. The first one at 108.3°C is mirrored in the TGA spectrum with a weight loss of 5.6%, representing the loss of uncoordinated and coordinated water. The second endotherm on the TDA is observed at 145.7°C, with a weight loss of

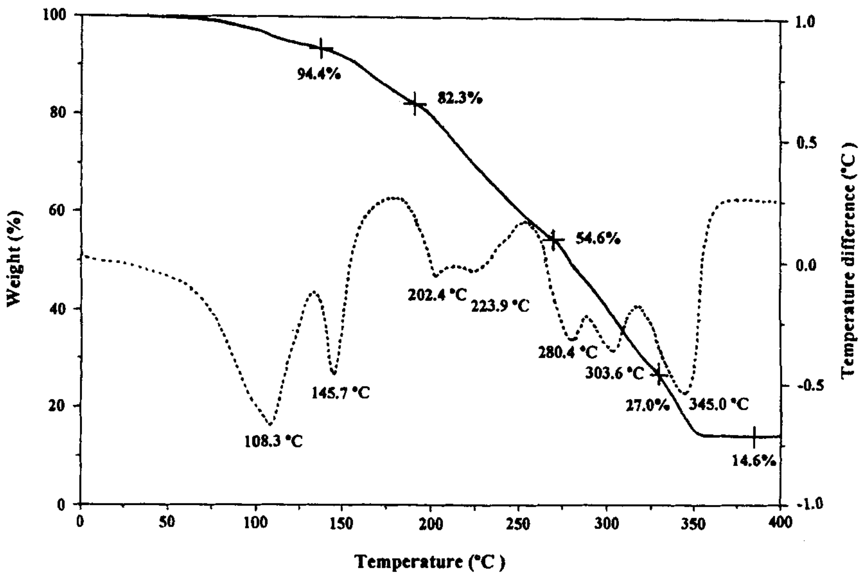

FIGURE 3 TGA/TDA curves for $[Cd(4,4'\text{-bpy})_2(H_2O)_2](BF_4)_2 \cdot 2(4,4'\text{-bpy}) \cdot (C_6H_6N_2O_2) \cdot 2H_2O$.

12.1%, corresponding an *o*-nitrobenzenamine molecule. The endotherms are at 202.4°C and 223.9°C (overlapping) are mirrored in the TGA plot with a total of weight loss of 27.7%, representing two uncoordinated 4,4′-bpy molecules. Endotherms at 280.4°C and 303.6°C with weight loss of 27.6% correspond to the loss of two coordinated 4,4′-bpy molecules. The last endotherm on the TDA curve is centred at 345.0°C; this feature is coupled with the simultaneous loss of 13.4% on the TGA curve, representing the decomposition of $Cd(BF_4)_2$ to CdF_2.

Supplementary Material

Hydrogen atom positions, thermal parameters and lists of observed and calculated structures are available from the authors on request.

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